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Systematic UHV-AFM experiments on Na nano-particles and nano-structures in NaCl

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Results of systematic AFM (atomic force microscopy) experiments on heavily and moderatly irradiated NaCl samples are presented. The sodium nanoparticles and structures of nanoparticles are poduced in sodium chloride during irradiation. The AFM images of the nanoparticles have been obtained in ultra high vacuum (UHV) in the non-contact mode with an Omicron UHV AFM/STM system. The sizes and arrangements of the observed particles depend on the irradiation conditions. The melting behaviour of the sodium nanoclusters has been studied for these samples by differential scanning calorimetry (DSC). A phenomenological model has been proposed which explains the observed behaviour by the existence of two different structural states in the population of sodium colloids. AFM measurements of heavily irradiated natural rock salt samples have revealed ring- and chain-like clusters (or agglomerates) of Na colloid particles.

1 Introduction

In this paper we present experimental observations of sodium colloids, which have been produced in bulk NaCl by the exposure of the samples to an intense beam of high-energy electrons from an electron accelerator. With direct AFM measurement of a freshly cleaved sample surface it is possible to observe sodium colloids, estimate their sizes and reveal colloids arrangements. Visualization of colloids and their arrangement combined with other methods (calorimetry, ESR, and SQUID) allow us to discover intricate features of small metallic particles.

2 Experiment

Several sets of NaCl mono-crystalline samples have been irradiated by means of 1.35 MeV electrons from a van de Graaff accelerator to doses between 5 and 150 GRad ($2x10^{17}$ and $6x10^{18}$ e^-/cm^2). Details of the experimental setup have been described in [1]. The irradiation dose in the irradiated sample has been calculated using standard procedures [2].

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The AFM results were obtained for these irradiated samples in ultra high vacuum (UHV) using an Omicron UHV AFM/STM system in the non-contact mode. To avoid chemical reactions between the radiolytic Na colloids and oxygen or water, the irradiated samples were cleaved, prepared and kept under UHV conditions prior to and during the experiments. Several AFM images have been obtained from different areas for each sample. The radii of the AFM tips, used in this investigation, have been estimated to be in the range between 20 and 30 nm, using scanning electron microscopy.
We have observed nano-size particles with height values, distributed over the range between 1 and 30 nm. Holes with different sizes have been observed on the cleaved surface as well. These holes might be associated with the traces of removed colloids, chlorine bubbles or voids. For heavily irradiated natural salt crystals ring- and chain- like clusters have been found on the sample surface. See Fig. 1.

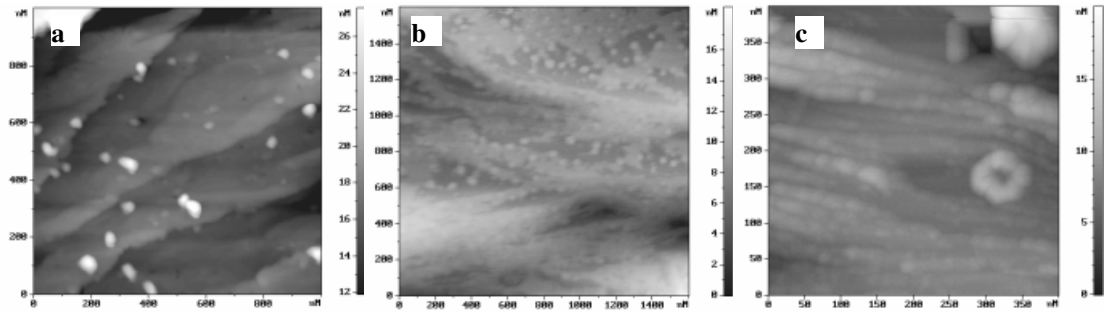

Fig. 1 AFM images. **a**) separate sodium particles, **b**) fractal structure, **c**) wire- and ring-like formation

DSC is very suitable method for the determination of the volume fraction of metallic Na produced inside the sample during the irradiation process. The latent heat of melting (LHM) of the Na colloids has been measured with a Perkin-Elmer DSC-7 system. The difference in heat flow between the irradiated sample and the reference sample (unirradiated NaCl) was measured during heating from 50ºC to 150ºC with a heating rate of 10ºC/min. The appearance of the LHM peaks in the 'DSC-spectrum' in this temperature interval is evidence for the presence of sodium colloids in the sample.

3 The melting properties

The study of the thermal properties and melting behavior of small sodium clusters has been carried out on potassium doped samples, which had been irradiated up to 5 – 20 Grad. We have observed two melting peaks in the 'DSC-spectrum' at 82 ºC and 92 ºC (see Fig. 2). Since DSC is an integral method, we can measure the thermal behaviour of the ensemble of different colloids. AFM allows us to find the distribution of colloid sizes.

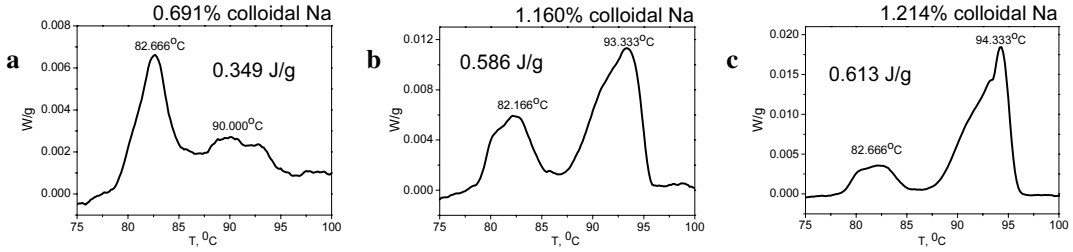

Fig. 2 DCS-spectrum of NaCl samples irradiated up to **a**) 5, **b**) 15 and **c**) 20 Grad respectively

The distributions of the particle sizes have been obtained from an analysis of the AFM images. Because of strong convolution effects, we have used the height of the nano-particles as the most reliable parameter for the evaluation of the colloid radii. The volume size distribution has been reconstructed from the

particles height distribution. Size distributions calculated for the samples with different irradiation doses show that distribution becomes wider and mean colloid size shifts toward larger sizes with increasing dose. At the same time the relative magnitude of the heat flow associated with the peak located at higher temperature increases. In [3] we have assumed that within the ensemble of colloids one can distinguish two different structural states, showing two different and well-defined melting temperatures (82 ºC and 92 ºC). To explain the observed melting behavior of the Na colloids a phenomenological model has been formulated, which attributes each melting peak to sodium colloids with either the *fcc* or the *bcc* crystal structure. It is likely that the surrounding NaCl-matrix forces the small sodium clusters to retain the *fcc* structure of the Na^+-sublattice. When small colloid grows larger than a certain radius, (a part of) its lattice eventually transforms to the *bcc* lattice structure of Na. In our phenomenological model R_{trans} was adjusted to reproduce the temperature dependence of the heat flow similar to what has been observed experimentally. The heat flow as a function of the temperature is given by

$$q(T) = C\rho_1(T)\int_0^{R_{trans}} \frac{4\pi}{3} r^3 F(r)dr + C\rho_2(T)\int_{R_{trans}}^{\infty} \frac{4\pi}{3} r^3 F(r)dr \qquad (1)$$

where $C = \frac{\beta_{DSC} H_f}{d_{NaCl} v_{Na}}$, β_{DSC} is the heating rate during the DSC measurements, d_{NaCl} is the density of NaCl, H_f is the heat of fusion per mole, $F(r)$ is the size distribution, $\rho_{1,2}(T)$ is the density probability function, depending of the melting temperatures of two different colloidal structures and v_{Na} is the molar volume of Na.

According to our estimations, during colloid growth the transition to the *bcc* structural state occurs at R_{trans} = 8 nm. This estimation doesn't contradict the experimental melting results obtained for free sodium clusters [4,5], where the transition radius has been evaluated to be about 3.5 or 4 nm, (cluster of about 10^4 atoms). We could expect a larger transition size for clusters embedded in a rigid NaCl-matrix compared with free Na-particles.

4 Colloid arrangement

In accordance with ESR data Na colloids in heavily irradiated NaCl samples form structures showing one-dimensional (1D) magnetic behaviour [6]. Direct AFM measurements have revealed ring- and chain-like clusters (or agglomerates) of Na colloid particles which are situated very close to each other (Fig. 1 (a,b)). Probably these structures are responsible for the anomalous magnetic properties observed for heavily irradiated samples. What factors cause the colloids to form clusters? The only 1D structures in crystals, which can provide nucleation sites for second-phase particles, are dislocation lines and dislocation loops. Therefore, it is likely that sodium colloids nucleate and grow along dislocations by absorption of F-centers. This explanation is in contrast with the existing models of radiolysis in NaCl [7, 8], which are based on the postulate that dislocations are biased toward absorption of H-centers compared to F centers, or more correctly, the dislocation bias for H centers is larger than the mean bias of the system. The discrepancy can be explained by the fact that the dislocation bias depends on arrangement of the dislocations and total sink strength. Real dislocation structures in irradiated materials are generally very inhomogeneous and contain various dislocation patterns such as pile-ups, walls etc. It is known that dislocation dipoles, dislocation walls and pile-ups of dislocation loops have a smaller bias than isolated edge dislocations [9]. The physical reason is the overlapping and mutual annihilation of elastic fields of individual dislocations in a pile-up. If the bias of a dense dislocation pattern is smaller than the mean bias of the overall system, than these structures absorb more F-centers than H centers. Excess F centers arriving at the dislocation in the pattern may migrate along the dislocation line and form colloids associated with the dislocation. At sufficiently high doses these colloids form densely-packed (chain- and ring-like)

1D structures. The mechanism of dislocation patterning is related to the mechanism of gas bubble growth. According to our model [8] the process of growth of Cl_2 gas bubbles is accompanied by punching dislocation loops. These loops are assumed to grow and form dislocation pile-ups.

It should be noted that in metals and alloys subjected to cascade damage dislocations are frequently found to be decorated with high densities of small dislocation loops. Mechanisms of dislocation decoration have been considered in [10] and in more detail in [11]. Decoration of the dislocations by self-interstitial loops is assumed to be due to the trapping of glissile loops in the strain field of the dislocation. Analogous effects are expected for NaCl, i.e. elastic interaction of nano-size prismatic dislocation loops, punched from growing bubbles, with isolated dislocation lines may result in accumulation of these loops near the dislocation lines. One may expect that the bias of these structures is smaller that the mean bias, which results in a preferential flow of F-centers to these structures. Dislocation forests are also decorated by colloids resulting in the formation of irregular fractal-like structures of colloids, which have indeed been observed in heavily irradiated NaCl by means of AFM.

The mechanism of colloid formation at dislocations can be illustrated as follows. Let the initial structure of the crystal consists of edge dislocations arranged in a 1D periodic pattern. Then, according to [9] the bias factor of such a system can be written as a function of the spatial coordinate x

$$\delta(x) = \frac{1}{\pi}\sqrt{\frac{\rho_{\min}}{\rho(x)}}\left[1 - \frac{1}{\pi}\sqrt{\frac{\rho_{\min}}{\rho(x)}}\ln\left(4\pi L_H\sqrt{\rho(x)}\right)\right]^{-1}\ln\left(\left|\frac{\Omega_H}{\Omega_F}\right|\right); \qquad L_H = \frac{\mu b\Omega_H(1+\nu)}{3\pi k_B T(1-\nu)} \tag{2}$$

where $\rho(x)$ is the dislocation density, $\rho_{\min}$ is the minimum dislocation density in the regions between dislocation pile-ups (see the caption for figure 3), $|\Omega_H/\Omega_F|$ is the ratio of the relaxation volumes of H-centers and F-centers, the remaining parameters have their usual meaning. Figure 3 shows the spatial dependence of the dislocation bias for H center absorption. It is seen that in the regions of high dislocation densities the bias factor is smaller than the mean bias, i.e. dislocations in this regions absorb preferentially F- centers, which may agglomerate to form colloidal structures of metallic nano-particles along the dislocations

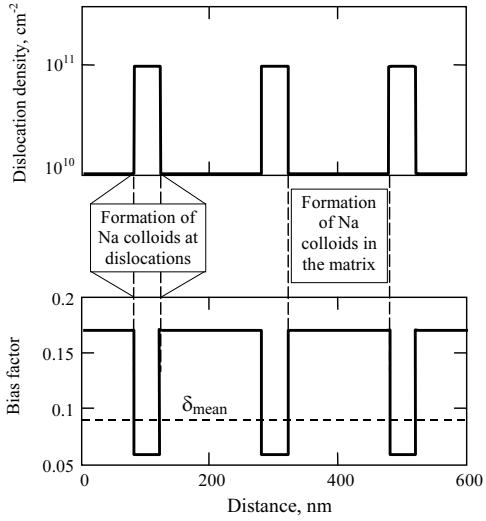

Fig. 3 The density (top) and the bias (bottom) of the periodic distribution of dislocations. The mean dislocation bias is given by $\delta_{mean} = \left(\int_0^{\lambda}\rho(x)dx\right)^{-1}\int_0^{\lambda}\delta(x)\rho(x)dx$, λ is the spatial period. $|\Omega_H/\Omega_F|$ = 1.67, L_H = 9 nm, $\rho_{\min} = 10^{10}$ cm^{-2} and $\rho_{\max} = 10^{11}$ cm^{-2}

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